

COATINGS

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GLASS PROTECTIVE PROCESS COATINGS FOR HEAT TREATMENT OF STEELS AND ALLOYS

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Scientific principles and principles for creating protective process coatings, which are complex composites with respect to the chemical and phase compositions, formed in heating metal blanks and parts are elaborated. Use of coatings protects against oxidation, dealloying, burnout of alloying elements, and gas saturation of the surface of parts and blanks of varying configuration and size.

Silicate glass protective process coatings are widely used in current nonoxidizing thermomechanical processing of metals and alloys.

Obtaining a high quality of the surface of steel and alloy parts after heat treatment is a function of its conditions, in particular, the chemical composition of the gas medium in which heating and subsequent quenching of the metal take place. Heating a metal in oxidizing air medium is accompanied by a number of negative results — oxidation, scaling, burnout of alloy components, dissolution of different gases in titanium, etc.

Of the methods of nonoxidizing heating, heat treatment of steels and alloys under a thin layer of a protective process coating (PPC) is effective.

It became possible to successfully solve the problems of creating protective coatings for heat treatment of steels and alloys due to the simultaneous study of not only the coatings themselves, but also the reaction of the coatings with the protected metals and alloys at high temperatures in aggressive media.

PPC have complex chemical and phase compositions and are formed on heating metal blanks and parts. The main distinctive feature of PPC is that they make it possible to obtain a metal surface of the same quality after high-temperature heating as after treatment with a cutter or in argon medium. Another advantage of the coatings is that they are formed on the surface of the metal while heating it in heat treatment, quenching, and normalizing. These coatings are the product of reactions that take place in the coating material under the effect of high temperatures and as a result of its contact with

the components of the metal and the components (oxygen, nitrogen, hydrogen, water vapors, etc.) of the ambient gas medium.

Formation processes and the protective effect of coatings were selected so that the temperature-time conditions of heat treatment of steel or alloy coincided in time with the formation of a continuous protective layer of coating and were determined by the composition of the coating, kinetics, composition and thickness of the alloy oxide film, thermal expansion coefficients of the substance of the coatings, the oxide film of the alloy and products of their reaction, and other heating conditions [1 – 3]. Consideration of these factors ensured spontaneous removal of the coating from the surface of the metal in the form of small scales (if the CLTE of the coating is lower than the corresponding CLTE of steel) or in the form of a continuous “blanket” if the thermal expansion of the coating was greater than for the support.

Creation of PPC was also based on notions concerning the possibility of constructing processes for synthesis of coatings and materials that resemble to some degree or are even similar to those in biological biosimilar systems, for example, in the structure and properties of the skin of living organisms, shed scale structures of reptiles, etc., i.e., coatings which are generated on the surface of the metal execute their vital function and then die (they separate from the surface of the metal and then no longer exist).

Compositions of high-temperature glasses and ceramic systems modified with thermodynamically stable oxide and high-melting oxygen-free compounds were selected for synthesis of PPC.

Five stages of thermogenesis of PPC were formed:

transfer of components (oxygen, water vapors) from the gas medium to the porous coating and to the alloy;

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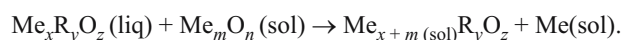
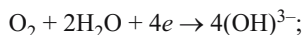
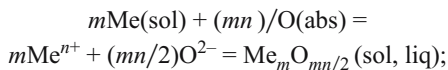
formation of a continuous (nonporous) molten coating layer;

heterogeneous reactions;

accumulation of reaction products on the boundaries of the coating and alloy, dissolution of the reaction products in the coating;

self-removal of the coating with the metal surface on cooling to room temperature.

The basic reactions are:



Protection of the surface from oxidation and dealloying during production of parts and blanks made of corrosion-resistant deformed steels and precision-cast parts made of corrosion-resistant, heat-resistant, and high-strength steels is one of the most pressing problems that can be solved with process coatings. Of the most important features of most glass-ceramics PPC compositions for corrosion-resistant steels, we note the multiphasicity, absence or low content of alkali metal oxides, and high content of high-melting ceramic additives.

Glass-forming frit is usually the basic component in coatings for protecting corrosion-resistant steels. The characteristics of the coatings are a function of its properties — viscosity, wettability, CLTE, softening point, and macro- and microstructure.

In developing coatings for protecting corrosion-resistant steels VNS-2, VNS-5, Kh18N10T and casting steels VNL-3, VNL-6, VNL-9, the ability of the coatings to dissolve the spinel oxide film formed on the surface of these steels during formation of the coating and consisting of high-melting chromium and nickel oxides, which caused the appearance of an intermediate layer on the coating – metal boundary that increased the efficacy of the protective effect of the coating, was taken into consideration. This is due to the formation of a highly viscous intermediate layer of glass and chromium and nickel oxides approximately 25 μm thick. This layer prevents intensive dissolution of iron and its oxides in enamel melt.

In heating steels VNS-2, VNS-5, Kh18N10T to 1100°C, VNL-3 to 1150°C, and VNL-8 with a coating to 1250°C, the oxidation rate did not exceed 0.1 $\text{mg}/(\text{cm}^2 \cdot \text{h})$, i.e., it was 270 times lower than in the unprotected samples (Fig. 1).

PPC No. 1 spontaneously separated from the surface of the protected parts in heat treatment during cooling due to the difference in the CLTE of the coating and the metal. Such a coating provides for nonoxidizing heating of corrosion-resistant steels VNS-2, VNS-5, Kh18N10T, and casting steels VNL-3, VNL-6, VNL-9, and ÉI-96LI. Heat treatment from the protected surface not only protected the surface of the

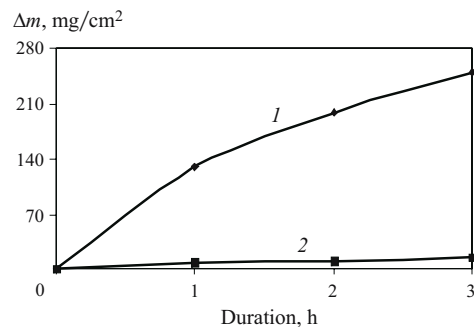


Fig. 1. Oxidizability of steel VNS-2 on heating to 1100°C with no coating (1) and with coating No. 1 (2).

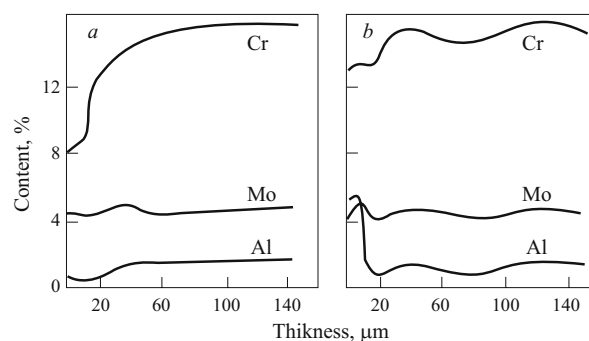


Fig. 2. Change in the mass content of elements in the surface layer of alloy XH435MVTYuBR after heating with no coating (a) and with coating (b).

steel from oxidation but also caused a more uniform structure of the surface layer (Fig. 2).

Formation of a defective surface layer on samples of iron-nickel alloy KhN45MVTYuBR with no coating was due to redistribution and burnout of alloy components in heating the alloy. In heating samples with protective coating No. 1 to 1150°C for 3 h, slight redistribution of the components was observed, but there was almost no dealloying of the surface layers of the alloy. The thickness of the defective layer of identical samples of alloy KhN45MVTYuBR with no coating was 15 – 20 times greater after quenching in similar conditions in barium chloride melt.

After heating unprotected samples of steel 90G28Yu9MVB to 1050°C and holding for 3 h, the carbon content decreased from 1.08 to 0.74%, the aluminum content went from 9.20 to 7.90%, and the manganese content dropped from 27.7 to 22%. The size of the carbon-poor layer was more than 0.45 mm, the manganese-poor layer was 0.3 mm, and the aluminum-poor layer was approximately 0.2 mm. When the steel with coating No. 1 was heated, there was almost no dealloying (Fig. 3).

To increase the protective parameters of the coatings for high-strength steels based on iron and improve their self-separation from the surface of the protected metal after heating, it was necessary to slow dissolution of iron oxides and other

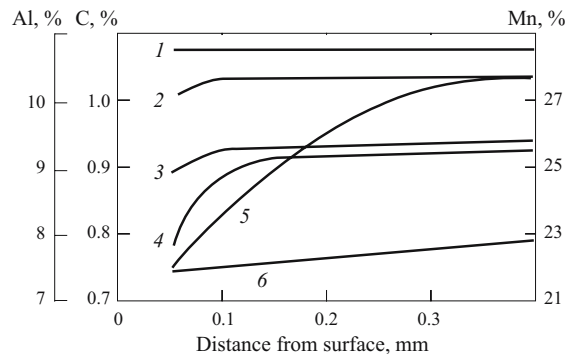


Fig. 3. Content of carbon (1, 6), manganese (2, 5), and aluminum (3, 4) in the surface layers of steel 90G28U9MVB with coating No. 1 (1–3) and with no coating (4–6) after treatment at 1050°C and holding for 3 h.

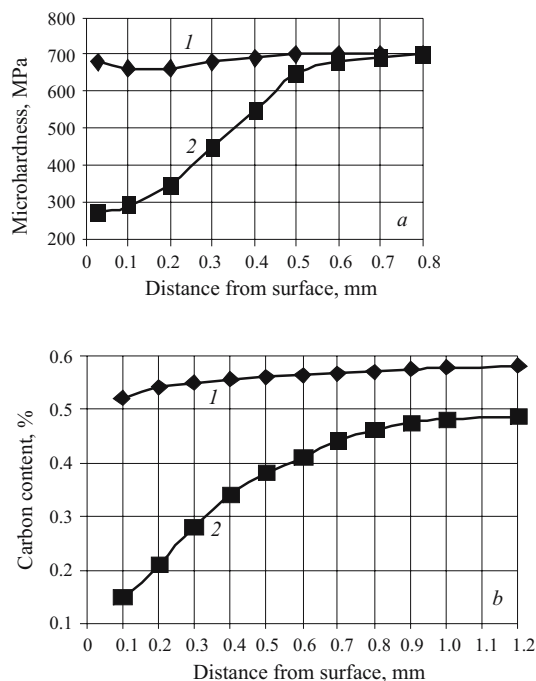


Fig. 4. Microhardness of the surface layer of steel 5KhNV after heating (a) and dependence of dealloying of steel 5KhNV on the heating conditions (b): 1) PPC No. 13; 2) with no coating.

oxides of variable-valence elements in the coating. It was possible to slow diffusion-chemical processes on the coating – metal boundary and increase the chemical inertness of the coating with respect to the protected support by reducing the glassy phase content in the protective layer.

PPC No. 7 was developed for quenching and normalizing high-strength steels ($\sigma_B \geq 1950$ MPa) VKS-9 and VKS-12; it protects steel from scaling and ensures the same mechanical properties after heat treatment in air medium as in treatment in inert argon medium. The coating does not cause corrosive cracking of the steel.

PPC No. 13 based on the $R_2O - B_2O_3 - SiO_2$ system was developed for punches made of steels 4Kh41MV3F, Kh12M, 5KhNV, and 5KhNM.

The samples of steel 5KhNM with and without coating No. 13 were treated with heat. The depth of the defective layer that appeared in heat treatment of the punches was determined by layer-by-layer chemical analysis of the surface layers (every 0.1 mm) and by measuring the microhardness over the section.

The protective properties of the coatings were evaluated visually after heating and with metallographic studies of the surface layers of the samples layer-by-layer chemical analysis for carbon. The degree of corrosive activity of frits was taken into consideration (Fig. 4).

Coating No. 13 was tested and introduced at a metal-processing plant.

Heat treatment of the punches was conducted in an electric furnace in the conditions: charging at 500°C, heating to 860°C in 24 h, holding at 860°C for 3 h, cooling in air for 15 min, quenching in oil; in tempering, heating to 500°C for 16 h, holding at 500°C for 4 h, cooling in air. The surface of the punch was light and the hardness was high after heat treatment.

The results obtained suggest that PPC No. 13 0.3 mm thick keeps the carbon in the surface layer of steel 5XNM at almost the initial level in heat treatment of the punches.

Coatings Nos. 7, 9, and 10, which are complex heterogeneous systems based on multiphase glass-ceramic compositions were developed for protecting high-temperature nickel alloys from oxidation during heat and gas-static treatment. The effectiveness of the protection ensures sufficiently high viscosity and density of the protective layers, chemical inertness, and formation of the coating at a lower temperature than the temperature of the onset of intensive oxidation of the alloy.

A feature of the structure of the oxidized surface of high-temperature nickel alloys is the presence of a defective dealloyed layer. PPC allows eliminating formation of this layer and obtaining a homogeneous structure of the γ' -phase with carbide intrusions. Such coatings protect parts made of high-temperature casting alloys from oxidation at heating temperatures up to 1250°C and make it possible to increase the quality and reliability of the parts (Fig. 5).

Titanium alloys are significantly oxidized and saturated with gas due to chemical activity in process heating so that irreversible losses in the form of scale are up to 10% and separation of the gas-saturated layers to shavings attains 50–80% of the mass of the initial blank. The presence of a brittle gas-saturated layer is the cause of crack formation in the finished parts and intermediate products so that mandatory removal of the solid gas-saturated layer in the intermediate processing stages is provided for by the process schemes for manufacturing articles made of titanium alloys. The layer contaminated by gases is removed by mechanical treatment or etching, which makes production much more expensive

due to the important amount of irreversible losses of alloys, high consumption of the hard-alloy cutter and scarce chemical reagents. In addition, removal of the gas-saturated layer by etching frequently involves undesirable hydrogen absorption of the metal.

In consideration of the reactivity of titanium alloys to oxidation and gas saturation in high-temperature heating, a series of PPC was developed for almost all process operations in heat treatment of titanium alloys (forging at 1200°C, heat treatment at 650–850°C, thermomechanical treatment, and isothermal stamping in conditions of superplasticity at temperatures up to 1050°C).

Glassy enamel coating No. 7 was developed for heat treatment of titanium alloys VT6 and VT14 to protect them and ensure mechanical properties identical to those in treatment in protective argon medium. Alloy VT-6S underwent biaxial extension and its mechanical properties are reported in Table 1.

The use of coating No. 7 in industry allowed conducting heat treatment of the welds in balloon balls, brackets, and other parts in ordinary furnaces instead of in furnaces with a controllable atmosphere, reduce argon consumption, and decrease the labor intensity of the process by 30% (Fig. 6).

In synthesis of PPC of high-melting, low-plasticity niobium, molybdenum, and tungsten alloys and colored zirconium, beryllium, and copper alloys, the problem of preventing oxidation and dealloying with formation of volatile oxides in the initial stages of formation of high-temperature coatings was solved.

The complex multicomponent composition of coatings Nos. 3, 13, and 15 ensured high temperature stability and spreadability and caused formation of a passivating layer with higher heat resistance than the heat resistance of the base on the alloy – coating interface due to counter diffusion. The PPC reliably protected the alloys during heating, reduced the depth of the defective layer by 10 times, and eliminated sublimation of molybdenum and tungsten oxides.

The kinetics of oxidation and gas saturation of zirconium alloys in heating is identical to the kinetics for titanium alloys. The effectiveness of protective coating No. 14M2 is especially markedly manifested by the decrease in the microhardness of the surface layers of the samples and intermediate products after complex heating in rolling and subsequent heat treatment. After hot rolling of blanks with no coating, the microhardness of the samples at a depth of 0.45 mm from the surface was greater than 2500 MPa, while the microhardness of samples with a coating at a depth of 0.02 mm from the surface were at the 2100 MPa level. The use of a coating in heating zirconium alloys decreased the concentration of oxygen in the surface layers by 20–30 times.

The studies of the kinetics of oxidation of beryllium at 750°C showed that the oxidizability of samples of beryllium both with and without a coating obeys a parabolic law. The

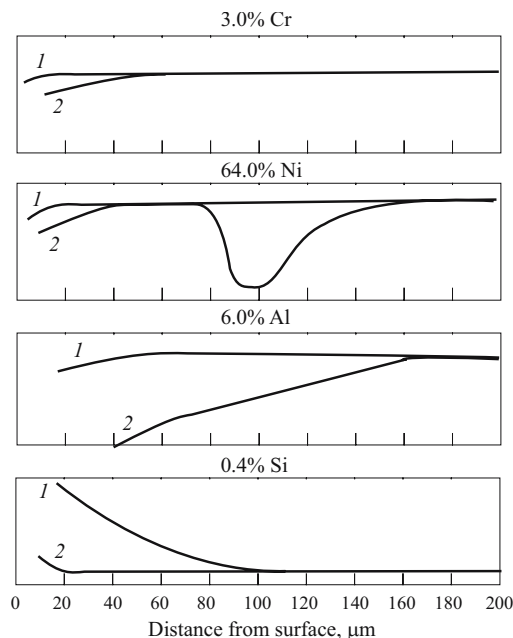


Fig. 5. Distribution of alloying elements in the surface layer of alloy ZhS26 with coating ÉVT-10 (1) and with no coating (2).

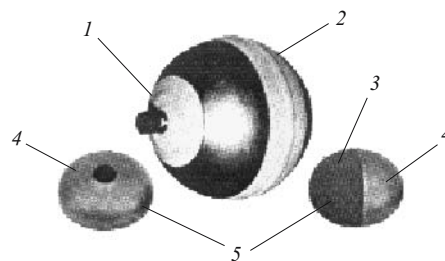


Fig. 6. Balloon ball after annealing of the weld with enamel: 1) VT-6S balloon; 2) weld under enamel; 3) with no enamel; 4) with enamel; 5) caps.

character of oxidation of beryllium changes when the temperature is increased to 1000°C, and the kinetics of oxidation of the samples with and without a coating differs significantly (Fig. 7).

PPC Nos. 6U, 3U, and 8U on beryllium in a complex with a passive film sharply decreased the rate of corrosion processes by preventing diffusion of aggressive components from the gaseous medium and the occurrence of chemical re-

TABLE 1

Sample	Heat treatment at 750°C		Tensile strength, MPa, of sample		Relative constriction after rupture, %
	duration	protective medium: argon	unnotched	notched	
Without enamel	1	Technical	1110	1160	5.2
Enamel No. 8	1	"	1160	1240	6.2
Without enamel	2	Refined	1110	1160	4.7
Enamel No. 8	2	"	1110	1150	4.6

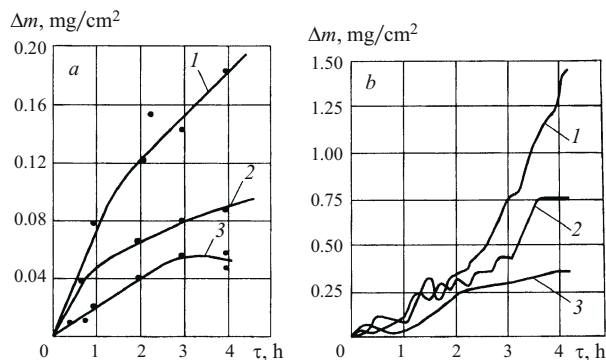


Fig. 7. Kinetics of oxidation of beryllium at 750°C (a) and 1000°C (b): 1) with no coating; 2) passive film; 3) passive film + enamel coating.

actions on the medium – coating – passive film – metal boundary under the effect of the high temperatures. They provide quality protection of beryllium from oxidation and sublimation of toxic beryllium compounds in heating to 1000°C.

With an increase in the heating temperature and holding time, the efficacy of the protective effect of the coating increases. This is due to the fact that beryllium and chromium diffuse into the coating and form compounds which are dis-

solved in the coating and increase its refractoriness and inertness.

The use of these coatings in heat treatment allows:

heating parts in ordinary furnaces instead of furnaces with a controllable atmosphere;

protecting parts of different shapes and large sizes from oxidation, gas saturation, decarbonization, and burnout of alloying elements;

saving metal by eliminating scaling and reducing allowances for mechanical processing;

reducing the laboriousness of sand blasting the parts by 3 – 5 times and mechanical treatment by 1.5 – 2 times;

reducing consumption of electricity, neutral gases, abrasive and cutting materials, and etching solutions by 20 – 30%.

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